Formal Transfers of Hydride from Carbon–Hydrogen Bonds. Attempted Generation of Molecular Hydrogen by Intramolecular Reduction of Protons Bound by 2,3-Dihydro-1,3-dimethyl-2-(8-quinolinyl)-1*H*-benzimidazole

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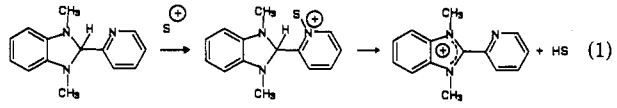
2,3-Dihydro-1,3-dimethyl-2-(8-quinolinyl)-1*H*-benzimidazole (**2**) is designed to bind electrophilic substrates and reduce them by an internal transfer of hydride. The intended binding site is the nitrogen atom of the quinoline ring, and the source of hydride is the carbon–hydrogen bond at C_2 of the dihydrobenzimidazole ring. Protons bind primarily to the nitrogen atom of the quinoline ring as expected, but they are not reduced to molecular hydrogen. Instead, protonation triggers a disproportionation reaction in which dihydrobenzimidazole is oxidized to benzimidazolium by an intermolecular transfer of hydride, and quinolinium is simultaneously reduced to tetrahydroquinoline. The failure of compound **2** to reduce protons to molecular hydrogen can be attributed primarily to unfavorable thermodynamics; the hydridic carbon–hydrogen and acidic nitrogen–hydrogen bonds of salt **2**-H$^+$ are inadequately activated, so alternative reactions are more rapid. Formation of hydrogen may also be disfavored kinetically because salt **2**-H$^+$ adopts an unsuitable conformation or because an appropriate trajectory for intramolecular protonation of the activated carbon–hydrogen bond is unattainable.

2,3-Dihydro-1,3-dimethyl-2-(2-pyridinyl)-1*H*-benzimidazole (**1**) contains a carbon–hydrogen bond activated as a formal donor of hydride by two antiperiplanar lone pairs in a dihydroaromatic ring, and the nitrogen atom of the pyridine ring can serve as a receptor site for electrophiles.[2] We hoped that the proximity of the activated carbon–hydrogen bond and the receptor site would allow compound **1** to bind electrophilic substrates S$^+$ and reduce them by an internal transfer of hydride (eq 1). Unfor-



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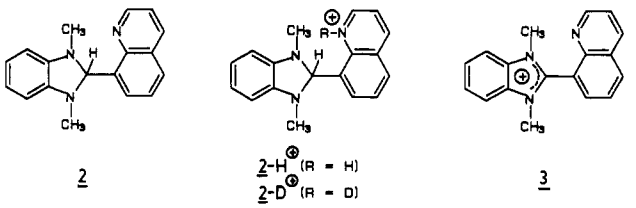
tunately, this novel reaction does not take place when dihydrobenzimidazole **1** is protonated (S = H). Molecular hydrogen is not formed, largely because the overall reaction is endothermic. Formation of hydrogen may also be disfavored for kinetic reasons, since salt **1**-H$^+$ prefers a conformation in which the hydridic carbon–hydrogen and acidic nitrogen–hydrogen bonds are not juxtaposed. In addition, an appropriate trajectory for intramolecular protonation of the activated carbon–hydrogen bond may be difficult to achieve.

As a result, two other reactions of salt **1**-H$^+$ are faster. One is a 1,2-shift of hydride from the activated carbon–hydrogen bond to the pyridinium ring, which produces an intermediate dihydropyridine. The other is direct heterolysis of the carbon–carbon bond between the dihydrobenzimidazole and pyridinium rings of salt **1**-H$^+$. To suppress these undesirable reactions, and to improve the trajectory for intramolecular protonation of the activated carbon–hydrogen bond, we decided to modify the receptor site of compound **1** by replacing the 2-pyridinyl group with an 8-quinolinyl group. The modified reagent, 2,3-dihydro-1,3-dimethyl-2-(8-quinolinyl)-1*H*-benzimidazole (**2**), and the salt **2**-H$^+$ produced by protonation of the quinolinyl nitrogen were expected to have conformations similar to those of their close relatives **1** and **1**-H$^+$, and the hydridic carbon–hydrogen and acidic nitrogen–hydrogen bonds of salt **2**-H$^+$ were expected to be approximately as reactive as those of salt **1**-H$^+$. However, a 1,2-shift of



2 **3**

hydride in compound **2**-H$^+$ can no longer produce a stable dihydroaromatic intermediate, and heterolysis of the carbon–carbon bond between the dihydrobenzimidazole and quinolinium rings cannot yield a highly stabilized ylide. We therefore hoped that compound **2**-H$^+$ could not avoid undergoing the reaction for which it was designed, internal reduction of the bound proton to molecular hydrogen.

Dihydrobenzimidazole **2** was easily synthesized in 72% yield by the condensation[3] of 8-quinolinecarboxaldehyde[4] with *N*,*N*′-dimethyl-1,2-benzenediamine.[5] Oxidation of compound **2** occurred readily, demonstrating the high reactivity of the activated carbon–hydrogen bond.[3,6,7] For example, oxidation with iodine in the presence of potassium carbonate produced 1,3-dimethyl-2-(8-quinolinyl)-benzimidazolium iodide (**3**) in 53% yield.[8]

Like dihydropyridinylbenzimidazole **1** and other close relatives,[2] compound **2** was expected to adopt a conformation in which the five-membered ring has an envelope shape and the hybridization of its two nitrogen atoms is shallowly pyramidal.[9] In addition, the quinoline ring

(1) Fellow of the Natural Sciences and Engineering Research Council of Canada.

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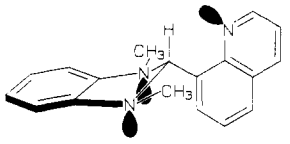
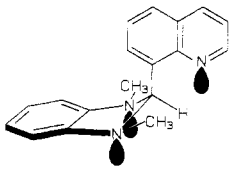
should be approximately perpendicular to the average plane of the five-membered ring. Unlike dihydropyridinylbenzimidazole **1**, however, compound **2** does not appear to favor a conformation similar to structure **2a**, in which the activated carbon–hydrogen bond is axial and antiperiplanar to two lone pairs. Conformation **2a** could

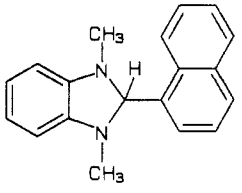


2a



2b

be rejected because the Bohlmann bands[11] between 2740 and 2550 cm^{-1} that are a conspicuous feature of the infrared spectrum of compound **1** are absent from the spectrum of compound **2** (KBr). This means that the lone pairs and the carbon–hydrogen bond at C_2 of the dihydrobenzimidazole ring cannot be antiperiplanar in the major conformers of compound **2**. We propose that compound **2** favors a conformation similar to structure **2b**, in which the carbon–hydrogen bond is equatorial.[7] Surprisingly, the closely related dihydrobenzimidazole **4**, prepared in 98% yield by the condensation of 1-naphthalenecarboxaldehyde with *N,N'*-dimethyl-1,2-benzenediamine, appears to prefer the alternative conformation **4a**, since its infrared spectrum (KBr) shows prominent Bohlmann bands at 2700–2550 cm^{-1}. These subtle differences suggest that several energetically similar conformations are accessible to substituted dihydrobenzimidazoles.



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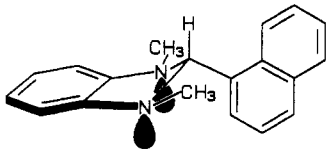

4a

Additional evidence that conformation **2b** is preferred came from the ^1H NMR spectrum of compound **2** ($CDCl_3$). The equatorial hydrogen at C_2 (δ 6.76) is much more deshielded than the axial activated hydrogens in dihydropyridinylbenzimidazole **1** (δ 5.11) and dihydronaphthylbenzimidazole **4** (δ 5.40), even though the methyl hydrogens of 8-methylquinoline (δ 2.83) are only slightly more deshielded than those of 2-methylpyridine (δ 2.57) and 1-methylnaphthalene (δ 2.62). Since hydrogens in carbon–hydrogen bonds antiperiplanar to lone pairs are characteristically shielded,[11a,12a] the striking downfield shift observed in compound **2** is consistent with a preference for a conformation like structure **2b**, in which the activated carbon–hydrogen bond is gauche to two lone pairs. Furthermore, the lone pair of the quinolinyl nitrogen in conformer **2b** may exert an important anisotropic deshielding effect on the nearby equatorial hydrogen.[13] If conformation **2b** is preferred, then the hydrogen at C_7 of the quinoline ring should be conspicuously deshielded by the other aromatic ring. In fact, this hydrogen appears δ 0.56 farther downfield than the corresponding hydrogen of 8-methylquinoline under conditions in which the other pairs of hydrogens have nearly identical chemical shifts.[14] As expected, the hydrogen at C_2 of the naphthalene ring of dihydrobenzimidazole **4** is even more strikingly deshielded by the axial lone pairs of the dihydrobenzimidazole ring, and it appears δ 1.40 downfield of the corresponding hydrogen of 1-methylnaphthalene.[15] Additional evidence supporting the hypothesis that dihydroquinolinylbenzimidazole **2** prefers conformation **2b** came from a ^1H NMR spectrum recorded at very low temperature (CHF_2Cl, −153 °C). Only one kind of *N*-methyl group was observed, indicating that symmetrical conformer **2b** is favored or that inversion of nitrogen in unsymmetrical conformers is extremely fast.

The quinolinyl nitrogen of dihydroquinolinylbenzimidazole **2** is therefore well positioned to bind reducible substrates near an activated carbon–hydrogen bond. In the preferred conformation of compound **2**, however, this carbon–hydrogen bond is not antiperiplanar to any lone pairs, so that it might be expected to be a poorer formal donor of hydride than the corresponding bond in dihydropyridinylbenzimidazole **1**.[12] Nevertheless, the rapid redox reaction of compound **2** with I_2 suggests that stereoelectronic factors are not critically important, or that the more reactive conformation **2a** is readily accessible. We were therefore optimistic that the favorable juxtaposition of a binding site and an activated carbon–hydrogen bond would allow dihydroquinolinylbenzimidazole **2** to bind protons and reduce them to molecular hydrogen.

The conjugate acid of quinoline (pK_a 4.9)[16] is slightly weaker than the conjugate acid of 1,2-benzenediamine (pK_a 4.5),[16] so protonation of compound **2** might be expected to produce quinolinium salt **2**-H^+. This expectation was supported by NMR spectroscopy, since the hydriodide formed in 98% yield by treating dihydroquinolinylbenzimidazole **2** with 1 equiv of hydrogen iodide showed strongly deshielded quinolinyl hydrogens and only moderately displaced *N*-methyl hydrogens. Remarkably, protonation shifted the activated hydrogen *upfield* by δ 1.49, largely because anisotropic deshielding by the lone pair of the quinolinyl nitrogen is eliminated in the hydriodide, and because protonation induces a profound conformational change. Several observations indicated that

(9) In contrast, molecular mechanics calculations[10] predict that the five-membered rings of dihydrobenzimidazoles **1** and **2** should be nearly planar and that the nitrogen atoms should be sp^2 hybridized. This discrepancy presumably arises because current versions of the molecular mechanics programs may systematically underestimate the pyramidalization of nitrogen in derivatives of aniline.

(10) These calculations used MMX87 (available from Serena Software, Bloomington, IN 47701) and MODEL (KS 2.9), an enhanced, graphics-interactive version of the MM2 molecular mechanics program: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127–8134. We thank Professor Kosta Steliou for implementation and helpful discussion of these programs.

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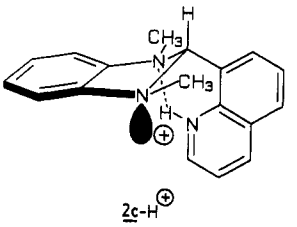
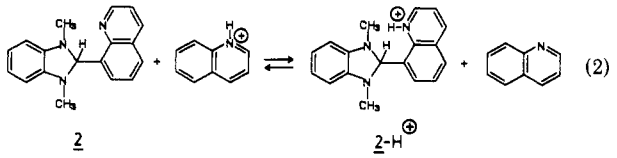
hydriodide **2**-H$^+$, like hydriodide **1**-H$^+$ and other closely related compounds,[2,17] incorporates an internal hydrogen bond and favors a conformation similar to structure **2c**-H$^+$.



2c-H$^+$

We expected this hydrogen bond to be fairly weak, since it is bent and since the nitrogens have imperfectly oriented lone pairs. As a result, the acidic hydrogen should interact more strongly with the nitrogen of the quinoline ring and iodide than with the nitrogens of the dihydrobenzimidazole ring. Nevertheless, comparison of the infrared spectra of deuterium-labeled salt **2**-D$^+$ and quinolinium iodide (hexachlorobutadiene mulls) provided evidence for additional hydrogen bonding in compound **2**-D$^+$. Its spectrum contains a broad band centered at 2205 cm^{-1} due to nitrogen–deuterium stretching, whereas the corresponding band of labeled quinolinium iodide appears at a slightly different frequency (2130 cm^{-1}). In addition, the chemical shift of the acidic hydrogen of hydriodide **2**-H$^+$ (δ 14.9, 0.085 M in CD_3CN) is not changed significantly by 16-fold dilution. These observations are consistent with the presence of an internal hydrogen bond in hydriodide **2**-H$^+$.

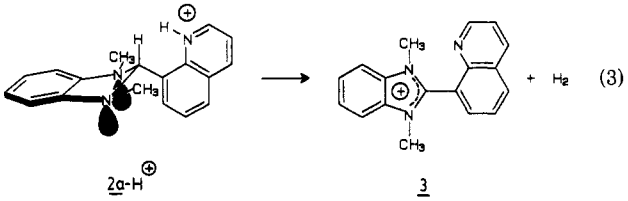
Since hydriodide **2**-H$^+$ is primarily a quinolinium salt, its pK_a should be similar to that of quinoline. The ^{1}H NMR spectrum of a dilute solution prepared by mixing equimolar amounts of dihydroquinolinylbenzimidazole **2** and quinolinium iodide (0.05 M, CD_3CN, 25 °C) showed well-resolved multiplets at chemical shifts that corresponded to a weighted average of those of compound **2** and salt **2**-H$^+$.[18] We calculate that the equilibrium constant for the proton exchange of eq 2 is approximately 4.5.



(2)

2 **2**-H$^+$

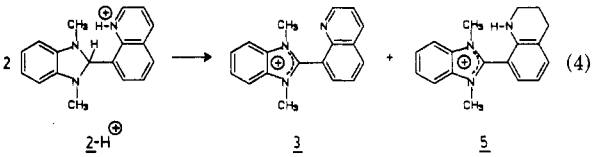
We hoped that gentle heating would break the internal hydrogen bond and let hydriodide **2**-H$^+$ adopt the presumably more reactive conformation **2a**-H$^+$. In this structure, the hydridic carbon–hydrogen and acidic nitrogen–hydrogen bonds are juxtaposed, perhaps facilitating the formation of molecular hydrogen and benzimidazolium iodide **3** (eq 3). In fact, pyrolysis of neat hydriodide **2**-H$^+$



(3)

2a-H$^+$ **3**

at 150 °C for 2$^1/_2$ h in vacuo cleanly yielded two products. One, isolated in 44% yield, was the expected quinolinylbenzimidazolium iodide **3**. Unfortunately, formation of compound **3** did not mean that hydriodide **2**-H$^+$ had lost molecular hydrogen, since persistent efforts to trap hydrogen during the thermolyses by passing effluent gases into a mixture of *trans*-stilbene and palladium on charcoal were unsuccessful.[2] The second product, isolated in 42% yield, was tetrahydroquinolinylbenzimidazolium iodide **5**. Examination of the crude pyrolysate by NMR spectroscopy showed that compounds **3** and **5** were formed in an approximately 1:1 ratio and that no other significant products were present. We conclude that protonation of the quinolinyl nitrogen of dihydrobenzimidazole **2** triggers a disproportionation reaction in which dihydrobenzimidazole is oxidized to benzimidazolium and quinolinium is eventually reduced to tetrahydroquinoline (eq 4).[19]



(4)

2-H$^+$ **3** **5**

Since the reduction potential of benzimidazolium (–1.85 V vs SCE) is more negative than that of quinolinium (–0.87 V),[20] this redox reaction is thermodynamically feasible. An intramolecular hydride transfer from the activated carbon–hydrogen bond of hydriodide **2**-H$^+$ to the reactive 2- and 4-positions of the quinolinium ring is geometrically improbable, so we believe that the disproportionation of eq 4 involves only intermolecular hydride transfers.[21,22]

The logical design of dihydroquinolinylbenzimidazole **2** successfully foils the undesired reactions that keep dihydropyridinylbenzimidazole **1** from binding protons and reducing them to molecular hydrogen. Unfortunately, however, its design incorporates a similar fatal shortcoming, and the carefully arranged collaboration of the receptor site and the activated carbon–hydrogen bond is again thwarted by a faster alternative reaction involving a pyridinium ring. We are continuing to study related compounds that bind reducible substrates close to an activated carbon–hydrogen bond but do not incorporate the undesirable features of dihydrobenzimidazoles **1** and **2**.

Experimental Section

Infrared (IR) spectra were recorded on Perkin-Elmer Model 710B and 783 spectrometers. Bruker WH-90 and WH-400 spectrometers were used to obtain ^{1}H nuclear magnetic resonance (NMR) spectra. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane (δ). Low-resolution mass spectra were recorded on a V.G. Micromass 12-12 quadrupole spectrometer using chemical ionization (CI) mass spectrometry or on a Kratos MS-50 TA spectrometer using fast atom bombardment (FAB) mass spectrometry. High-resolution mass spectra were recorded on a Kratos MS-50 TA spectrometer using fast atom bombardment (FAB) mass spectrometry. Galbraith Laboratories,

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(21) To avoid the direct interaction of two cationic molecules, the disproportionation of eq 4 may be mediated by hydride transfer from small amounts of free base **2** derived from hydriodide **2**-H$^+$ by the loss of hydrogen iodide.
(22) Various attempts to suppress the undesired disproportionation of eq 4 were unsuccessful. For example, hydriodide **2**-H$^+$ could not be induced to liberate molecular hydrogen even when dilute solutions (0.002 M) in 95% ethanol were warmed at 50 °C for 90 h. This demonstrates that intermolecular hydride transfer is faster than intramolecular formation of hydrogen in hydriodide **2**-H$^+$ even at low concentrations. In addition, replacing iodide in salt **2**-H$^+$ by hexafluorophosphate had no important effect on the thermolyses. We also observed that pyrolyses of neat hydriodide **2**-H$^+$ in vacuo at temperatures as high as 270 °C gave similar results, although substantial amounts of benzimidazoles appeared to be formed by subsequent demethylation of compounds **3** and **5**.

Knoxville, TN, performed all elemental analyses. Melting points were recorded on a Thomas-Hoover capillary apparatus and are not corrected. Acetonitrile was dried by distillation from P_2O_5, and benzene was dried by distillation from sodium. Solvents were deoxygenated by sparging with dry argon. All other reagents used were commercial products of the highest purity available.

2,3-Dihydro-1,3-dimethyl-2-(8-quinolinyl)-1*H*-benzimidazole (2). A solution of *N,N'*-dimethyl-1,2-benzenediamine[5] (90.8 mg, 0.667 mmol), 8-quinolinecarboxaldehyde[4] (123 mg, 0.783 mmol), and (1*S*)-(+)-10-camphorsulfonic acid (6 mg) in benzene (12 mL) was heated at reflux for 48 h under N_2 in an apparatus fitted with a Dean–Stark trap containing 4-Å molecular sieves. The mixture was then extracted with cold, deoxygenated 5% aqueous NaOH and water, the organic phase was dried, and solvent was removed by evaporation under reduced pressure. Recrystallization of the residue from methanol yielded orange prisms of 2,3-dihydro-1,3-dimethyl-2-(8-quinolinyl)-1*H*-benzimidazole (**2**): 133 mg, 0.483 mmol (72.4%); mp 132–133 °C; IR (KBr) 3060, 2955, 2860, 2800, 1600, 1575, 1500, 1340, 1290, 1120, 1015, 805, 785, 735, 640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.65 (s, 6 H), 6.47 (dd, 2 H), 6.76 (s, 1 H), 6.75 (dd, 2 H), 7.46 (dd, $J_{2,3}$ = 4.14 Hz, $J_{3,4}$ = 8.30 Hz, H_3), 7.69 (dd, $J_{5,6}$ = 8.10 Hz, $J_{6,7}$ = 7.22 Hz, H_6), 7.88 (dd, $J_{5,6}$ = 8.10 Hz, $J_{5,7}$ = 1.40 Hz, H_5), 8.23 (dd, $J_{2,4}$ = 1.79 Hz, $J_{3,4}$ = 8.30 Hz, H_4), 8.36 (dd, $J_{5,7}$ = 1.40 Hz, $J_{6,7}$ = 7.22 Hz, H_7), 8.97 (dd, $J_{2,3}$ = 4.14 Hz, $J_{2,4}$ = 1.79 Hz, H_2); mass spectrum (CI, isobutane), *m/e* 275, 260, 147. Anal. Calcd for $C_{18}H_{17}N_3$: C, 78.52; H, 6.22; N, 15.26. Found: C, 78.92; H, 6.51; N, 15.23.

1,3-Dimethyl-2-(8-quinolinyl)benzimidazolium Iodide (3). A stirred mixture of 2,3-dihydro-1,3-dimethyl-2-(8-quinolinyl)-1*H*-benzimidazole (**2**; 120 mg, 0.436 mmol) and K_2CO_3 (64.2 mg, 0.465 mmol) in methanol (5 mL) was treated at 25 °C with a solution of I_2 (123 mg, 0.485 mmol) in methanol (20 mL), added dropwise during 90 min. The resulting mixture was stirred at 25 °C for 12 h, and then volatiles were removed by evaporation under reduced pressure. The product was extracted with chloroform, and solvent was removed from the filtered extracts by evaporation under reduced pressure. Recrystallization of the residue from dichloromethane/benzene provided 1,3-dimethyl-2-(8-quinolinyl)benzimidazolium iodide (**3**) as an off-white solid: 92.4 mg, 0.230 mmol (52.8%); mp 284 °C dec (lit.[8] mp 282–284 °C); IR (KBr) 3030, 2970, 1585, 1520, 1495, 1490, 1480, 840, 795, 765 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 3.91 (s, 6 H), 7.5–8.2 (m, 6 H), 8.30 (m, 2 H), 8.86 (dd, 1 H), 9.18 (d, 1 H); ^1H NMR (90 MHz, CD_3CN) δ 3.78 (s, 6 H), 7.6–8.1 (m, 6 H), 8.24 (dd, 1 H), 8.51 (m, 2 H), 8.90 (dd, 1 H); mass spectrum (FAB, glycerol), *m/e* 274. Anal. Calcd for $C_{18}H_{16}IN_3$: C, 53.88; H, 4.02; N, 10.47. Found: C, 54.04; H, 4.03; N, 10.36.

2,3-Dihydro-1,3-dimethyl-2-(1-naphthyl)-1*H*-benzimidazole (4). 2,3-Dihydro-1,3-dimethyl-2-(1-naphthyl)-1*H*-benzimidazole (**4**) was prepared by a procedure similar to the one described for dihydroquinolinylbenzimidazole **2**. Recrystallization from 95% ethanol provided compound **4** in 74% yield: mp 158–159 °C; IR (KBr) 3065, 2960, 2860, 2800, 1605, 1500, 1390, 1290, 1120, 1055, 1020, 795, 780, 735, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.54 (s, 6 H), 5.40 (s, 1 H), 6.50 (dd, 2 H), 6.77 (dd, 2 H), 7.40 (t, H_6), 7.45 (br s, H_3), 7.47 (t, H_7), 7.60 (br s, H_4), 7.87 (d, H_5), 7.89 (d, H_8), 8.66 (br s, H_2); mass spectrum (CI, isobutane), *m/e* 274, 147.

Hydriodide 2-H$^+$ of 2,3-Dihydro-1,3-dimethyl-2-(8-quinolinyl)-1*H*-benzimidazole (2). A solution of 2,3-dihydro-1,3-dimethyl-2-(8-quinolinyl)-1*H*-benzimidazole (**2**; 71.1 mg, 0.258 mmol) in ether (3 mL) was stirred at 25 °C under N_2 and treated dropwise with hydriodic acid (5%, 0.4 mL). The precipitated solid was separated by centrifugation, washed with cold ethanol (1 mL), and dried in vacuo at 25 °C. This yielded a pure sample of hydriodide **2**-H$^+$: 102 mg, 0.253 mmol (98.1%); mp 161 °C dec; IR (KBr) 3150–2550 (br), 2450 (br), 1635, 1595, 1545, 1490, 1275, 780, 765, 755 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 2.60 (s, 6 H), 5.27 (s, 1 H), 6.75 (dd, 2 H), 6.89 (dd, 2 H), 8.03 (t, $J_{5,6}$ = 8.42 Hz, $J_{6,7}$ = 7.22 Hz, H_6), 8.07 (dd, $J_{2,3}$ = 5.52 Hz, $J_{3,4}$ = 8.43 Hz, H_3), 8.19 (dd, $J_{5,7}$ = 1.30 Hz, $J_{6,7}$ = 7.22 Hz, H_7), 8.43 (dd, $J_{5,6}$ = 8.42 Hz, $J_{5,7}$ = 1.30 Hz, H_5), 9.02 (dd, $J_{2,3}$ = 5.52 Hz, $J_{2,4}$ = 1.56 Hz, H_2), 9.22 (dd, $J_{2,4}$ = 1.56 Hz, $J_{3,4}$ = 8.43 Hz, H_4); mass spectrum (CI, isobutane), *m/e* 275, 260, 147; high-resolution mass spectrum (FAB, thioglycerol), calcd for $C_{18}H_{18}N_3$ 276.1501, found 276.1430.

Pyrolysis of Hydriodide 2-H$^+$. Hydriodide **2**-H$^+$ (55.1 mg, 0.137 mmol) was sealed in vacuo in a Pyrex tube and heated at 150 °C for $2^1/_2$ h. Careful fractional crystallization of the pyrolysate from dichloromethane/benzene precipitated 1,3-dimethyl-2-(8-quinolinyl)benzimidazolium iodide (**3**; 23.9 mg, 0.0596 mmol, 43.5%), which was identified by its IR and ^1H NMR spectra. Removal of solvent from the mother liquors by evaporation under reduced pressure left a residue of 1,3-dimethyl-2-(1,2,3,4-tetrahydro-8-quinolinyl)benzimidazolium iodide (**5**): 23.3 mg, 0.0575 mmol (42.0%); IR (solid film) 3240, 1600, 1515, 1485, 1475, 1285, 915, 740, 725 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.91 (quint, 2 H), 2.83 (t, 2 H), 3.4 (m, 2 H), 3.96 (s, 6 H), 6.66 (t, 1 H), 6.86 (d, 1 H), 7.22 (d, 1 H), 7.66 (s, 4 H); high-resolution mass spectrum (FAB, glycerol), calcd for $C_{18}H_{20}N_3$ 278.1657, found 278.1625. Benzimidazolium iodide **5** was identical by IR and NMR with a sample independently synthesized in low yield by the reduction of benzimidazolium iodide **3** with Raney nickel.[23]

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